Excited state LO phonons in quantum dots

著者	Masumoto Y, Zhao J L, Kanno A
内容記述	Physics of semiconductors 2002 : proceedings of the 26th International Conference on the Physics of Semiconductors held in Edinburgh, UK, 29 July-2 August 2002
発行年	2002
URL	http://hdl.handle.net/2241/98357

Excited state LO phonons in quantum dots

Y Masumoto, J L Zhao and A Kanno

Institute of Physics, University of Tsukuba, Tsukuba 305-8571, Japan

Abstract. The size dependence of the excited state-longitudinal optical (LO) phonons and exciton states for CuBr quantum dots (QDs) embedded in glass and NaBr crystals in the intermediate confinement regime and CuI QDs embedded in glass in the strong confinement regime was studied by means of persistent spectral hole burning spectroscopy. The phonon-exciton coupled states were clearly observed in CuBr QDs embedded in glass when the LO phonon energy is close to the energy difference between the ground and excited state. The energy softening of the LO phonons was observed in CuBr and CuI QDs similarly to CuCl QDs and was explained in terms of the phonon renormalization by Fröhlich coupling.

1. Introduction

The elementary excitations of small quantum dots (QDs) containing a few hundreds of atoms are expected to modify strongly the lattice vibrational frequencies due to carrier confinement and resulting strong exciton-phonon interaction similarly to the lattice vibration in the excited state of many molecules and localized centers in solids [1]. The modification of the vibrational frequency in the electronic excited state is so unique for molecules and localized centers in solids that the presence of the modification of the vibrational frequency in the electronic excited state of small-sized QDs shows a characteristic of quantum dots of their molecular-nature. Recently, the energy softening of the longitudinal optical (LO) phonon by 8% was observed in persistent spectral hole burning (PSHB) and resonant photoluminescence spectra of 2.5 nm-radius CuCl QDs, typical QDs in the weak confinement regime [2-4]. In contrast to 25.6 meV LO phonon in the ground states observed in Raman scattering and resonant photoluminescence spectra, 23.5 meV LO phonon was observed in the excited state by means of PSHB and resonant photoluminescence. The exciton-phonon coupled states were clearly observed as a result of strong Fröhlich interaction in both quantum spheres and quantum cubes, when the energy of the LO phonon is close to the energy spacing between the ground and excited exciton quantum states [2,4]. The LO phonon softening in the excited state CuCl QDs was also observed by means of quantum beats in the time domain [5] and two-photon-excited resonant luminescence in the spectral domain [6]. Theoretically, the energy softening was described in terms of the phonon renormalization in the presence of a single exciton in spherical QDs [2,6,7]. The theory predicted further the LO phonon renormalization in the excited QDs not only in the weak confinement regime but also in the strong confinement regime [6,8].

In this work, we extend the study of phonon softening to QDs in the intermediate and strong confinement regimes from QDs in the weak confinement regime. We study in detail the size dependence of the excited state-LO phonons and exciton states for CuBr QDs embedded in glass and NaBr crystals in the intermediate confinement regime and CuI QDs embedded in glass in the strong confinement regime by means of PSHB spectroscopy. We successfully found the mixing of the LO phonon with exciton when the energy of the LO phonon approaches the energy spacings between the ground and excited states for CuBr QDs and the energy softening of LO phonon in both CuBr QDs and CuI QDs.

2. Theoretical background

Using an adiabatic potential model and the Hamiltonian described below, one can understand the reason why the LO phonon softening and anticrossing between LO phonon energy and quantized excitonic or electronic transition energy take place [2,4,7,8]. The adiabatic potential model itself has been used frequently for the electronic states of molecules and localized centers in solids. The exciton (electron)-phonon Fröhlich Hamiltonian is described by

$$H = \sum_i E_i c_i^+ c_i + \sum_{nlm} \Omega a_{nlm}^+ a_{nlm} + \sum_{ijnlm} \gamma_{nlm}^{ij} c_i^+ c_j (a_{nlm}^+ + a_{nlm}), \quad (1)$$

where c_i and E_i denote the annihilation operator and energy of the i-th exciton (electron or hole) state, a_{nlm} is the phonon annihilation operator for the n-th phonon mode of angular momentum of l, γ_{nlm}^{ij} is the coupling constants which is inversely proportional to square root of the product of $\kappa = \varepsilon_0 \varepsilon_\infty / (\varepsilon_0 - \varepsilon_\infty)$ and radius of dots R, and Ω is the LO phonon energy. The second order perturbation treatment of the exciton (electron or hole)-phonon Fröhlich interaction described in the third term in Eq. (1) gives the additional parabolic term $\sum_{nlm} \delta\Omega a_{nlm}^+ a_{nlm}$ and phonon energy change, if the interaction is strong, where

$$\delta\Omega = -\sum_{i \neq 0} \frac{\left|\gamma_\nu^{0i}\right|^2 2(E_i - E_0)}{(E_i - E_0)^2 - \Omega^2}. \quad (2)$$

Here 0 denotes the exciton (electron or hole) ground state.

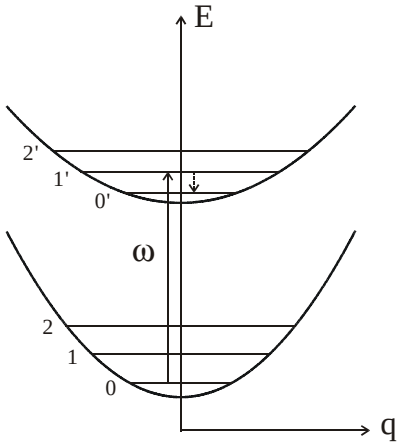

Figure 1. The excitation and relaxation processes involved in the persistent spectral hole burning with the emission of LO phonon in the configuration coordinate model. LO phonon energy in the electronic excited state is smaller than that in the electronic ground state.

The unique feature of quantum dots is that quantized excitonic (electronic) energy spacing can match with LO phonon energy for small sized dots. Then the phonon energy change is considerable and can be detected experimentally. For CuCl dots whose radii are smaller than 5 nm, Eq. (2) gives negative value and LO phonon energy shows softening. As a result, the adiabatic potential model for quantum dots is described as is in Fig.1, where LO phonon energy in the electronic excited state Ω^* is smaller than that in the electronic ground state Ω.

Around the resonance between the phonon energy and excitonic (electronic) energy spacing, the perturbation theory fails and two renormalized new modes appear. This explains the anticrossing behaviour. The almost parallel story holds for exciton-phonon interaction in the weak confinement case and electron or hole-phonon interaction in the strong confinement case except the coupling. The coupling for the strong confinement case multiplied by a factor $[1/(1+\alpha_e/4)^2 - 1/(1+\alpha_h/4)^2]$ corresponds to that for the weak confinement case, where $\alpha_{e(h)} = (\pi m_{e(h)} a_B / MR)^2$, a_B is the exciton Bohr radius in the bulk crystal, $M = m_e + m_h$ is the exciton translational mass and $m_{e(h)}$ is the electron (hole) mass [8].

3. Experimental

CuBr and CuI QDs used in the experiment were embedded in glass or NaBr crystals. The size of the QDs was controlled by heat treatment with different temperature and time. The samples were directly immersed in superfluid helium at 2 K in an optical cryostat. A narrow-band dye laser pumped by the third harmonics of the output of a Q-switched Nd^{3+}: YAG laser (355 nm) was used as a pump source. The pulse duration and repetition rate were 5 ns and 30 Hz, respectively. The laser dyes used in the experiment are Exalites 384, 389, 398, 404, and 411. The spectral linewidth was about 0.014 meV. A halogen lamp was used as a probe source. The PSHB spectrum was measured as follows: First, the absorption spectrum was obtained and the sample was exposed to dye laser pulses to burn a persistent spectral hole at excitation energy. Then, the absorption spectrum was measured again after the laser exposure was stopped. The absorption spectral change $-\Delta\alpha d$ is defined as the difference between the spectra before and after the laser exposure. The subsequent measurements were performed at the new position of the samples and were not carried out at the position burnt previously. The transmitted light of the samples was detected by a liquid-nitrogen cooled charge-coupled device in conjunction with a 75-cm spectrometer involving a 1800 grooves/mm grating operated in the first order of diffraction. The spectral resolution of the experiment was about 0.3 meV.

4. Experimental results and discussion

4.1. Excited state-LO phonons and exciton-phonon coupled states in CuBr QDs in glass

Phonons observed in the PSHB spectroscopy are unique, because it selectively sees the optical phonons in the electronic excited states as a pseudophonon wing at low temperatures [2]. The excitation and relaxation processes involved in the PSHB with the emission of LO phonon in the configuration coordinate model is described in Fig. 1. On the other hand, resonant luminescence observes the optical phonons both in the electronic excited states and in the electronic ground state, and Raman scattering observes the optical phonons in the electronic ground state. To observe the LO phonons in the electronic excited states, the PSHB spectroscopy is superior to others. Fortunately, PSHB phenomena have been observed in CuBr QDs in the weak and intermediate confinement regimes [9,10].

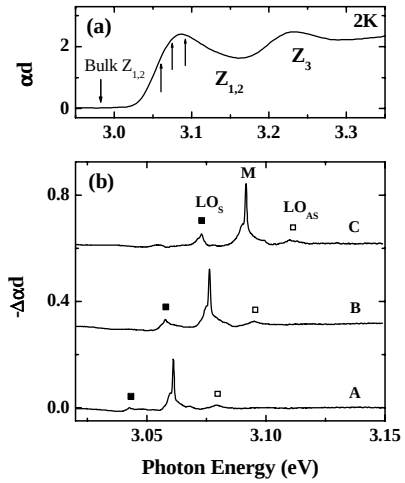

Figure 2. Absorption (a) and PSHB spectra (b) of CuBr QDs in glass with an average radius of 2.4 nm. The excitation energies for spectra A, B, and C are 3.0611, 3.0763, and 3.0916 eV, respectively. The excitation density is 100 nJ/cm^2 and exposure time is 5 minutes.

Figure 2 shows the absorption and PSHB spectra of CuBr QDs in glass with an average radius of 2.4 nm. The $Z_{1,2}$ exciton absorption band of CuBr QDs is inhomogeneously broadened due to the size distribution. In comparison with the lowest exciton resonance ($Z_{1,2}$ = 2.9640 eV at 2 K) of the bulk CuBr crystal, the blue shift of the $Z_{1,2}$ exciton absorption peak of the CuBr QDs was determined to be about 126 meV. As seen in Fig. 2(b), a sharp main hole marked by M with asymmetric acoustic phonon sidebands is observed at the excitation energy. The Stokes and anti-Stokes-side phonon bands labelled by LO_S and LO_{AS} are clearly seen at the low and high-energy side of the main hole and LO_S is the pseudophonon wing. The Stokes shifts between the phonon sideband holes and the main hole were obtained to be about 18.6 meV. The energies of the LO and transverse optical (TO) phonons in the bulk CuBr are 21.1 and 17.0 meV [11], respectively, which were measured by Raman scattering. Recently, by resonant hyper-Raman scattering, the energy of LO phonon in the CuBr QDs in glass was measured to be 20.3 meV which was almost the same as LO phonon in the bulk CuBr crystal [12-15]. The energy of the LO phonon side bands for small 2.4 nm-radius CuBr QDs in glass was found to be lower than that of the bulk CuBr crystal by 2.5 meV (12%). The LO phonon softening observed in CuBr QDs by the PSHB spectroscopy is considered as the LO phonon renormalization in the presence of a single exciton in spherical QDs, in analogy with the LO phonon softening observed in CuCl QDs [2,4-6].

Further, we study systematically the LO phonons in different size CuBr QDs to clarify the mixed mode composed of phonon and exciton. Figures 3(a) and 3(b) show the absorption and PSHB spectra of CuBr QDs with different average radii. By increasing the size of the QDs, the $Z_{1,2}$ exciton absorption band is shifted to the low energy side and is split into two peaks probably due to the strain effect. The energy of the LO phonon hole for smaller CuBr QDs was estimated to be about 18.6 meV. A satellite hole marked by E_1 was observed in the PSHB spectra of larger size dots. The Stokes shift of the satellite hole becomes small gradually when the dot size increases. Thus the satellite hole is considered to come from the hole burning of the ground state (1*S*) under excitation of the first excited state (1*P*) of the quantum confined excitons in the nearly spherical CuBr QDs.

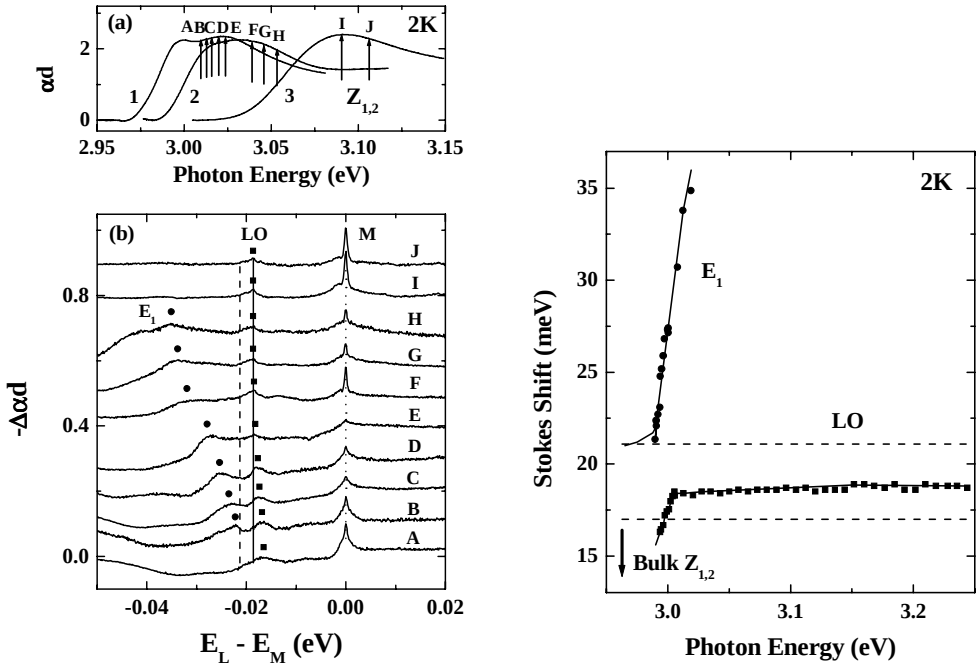

Figure 3. Absorption (a) and PSHB spectra (b) of CuBr QDs in glass. The average radii for samples 1, 2, and 3 are 10.5, 5.0, and 2.4 nm. The excitation energies for spectra A, B, C, D, E, F, G, H, I, and J are 3.0094, 3.0130, 3.0167, 3.0203, 3.0242, 3.0388, 3.0463, 3.0537, 3.0916, and 3.1073 eV, respectively. The excitation density is 100 nJ/cm^2 and exposure time is 5 minutes. The solid and dashed lines represent the energies of the LO phonons in the ground state and excited state of the excitons. (c) Stokes shifts of the satellite holes E_1 and LO in CuBr QDs in glass as a function of the observed photon energy of the respective hole structures. The dashed line represents the energies of LO and TO phonons in a bulk CuCl crystal. The solid lines show a guide for eyes.

As seen in Fig. 3(b), the holes E_1 and LO become close to each other when the dot size is increased. When the LO phonon energy of CuBr QDs in glass approaches the energy difference between the 1*S* exciton and 1*P* exciton, the LO phonon energy clearly shows an anticrossing with the Stokes shift of the hole E_1 at an energy of about 2.9960 eV. We consider 1*P* exciton can be excited and can be relaxed to 1*S* exciton with the emission LO phonon with $l = 0$, because CuBr QDs are not perfectly spherical. An anticrossing of the phonon energy with the separation between ground state exciton and excited state exciton is clearly observed in Fig. 3(c). The experimental result indicates that the interaction of the LO phonon with the exciton in CuBr QDs in glass results in the formation of the exciton-phonon coupled modes at exciton-phonon resonance, which is similar to those observed in CuCl QDs [2,4-6].

4.2. Excited state LO phonons and exciton states in CuBr QDs in NaBr crystals

Figures 4 (a) and (b) show the absorption and PSHB spectra of CuBr QDs in NaBr crystals at 2 K. Many satellite holes are observed at not only the low-energy side but also the high-energy side of the main hole M. The Stokes shift of the sharp LO phonon hole in CuBr QDs in NaBr crystals was determined to be 17.6 meV, which is lower than that of the bulk CuBr (21.1 meV) by 3.5 meV (17%) but larger than the TO phonon energy. The

hole L_1 is a dominant satellite hole in the PSHB spectra. The Stokes shifts of the satellite holes L_1 and LO as a function of the photon energy are plotted in Fig. 4(c). The Stokes shift of the hole L_1 is considered as the energy difference between the ground (1*S*) and an excited (1*P*) state of the quantum confined exciton. If the energy of the LO phonon energy is close to the energy difference, the LO phonon is expected to mix with the excited state of the exciton, which should lead to the formation of the exciton-phonon coupled states. However, we have not obtained large-sized CuBr QDs in NaBr crystals which permit us to observe the anticrossing region. The exciton-phonon coupled states were clearly demonstrated only in CuBr QDs in glass and were not observed in CuBr QDs in NaBr crystals although the LO phonon softening was observed in both cases.

4.3. LO phonon modes in CuI quantum dots

PSHB phenomena have been observed in CuI QDs in the strong confinement regime [16]. Figures 5 (a) and (b) show the absorption and PSHB spectra of CuI QDs in glass. A broad $Z_{1,2}$ exciton peak is observed in the absorption spectrum of CuI QDs. As seen in Fig. 5(b), the Stokes and anti-Stokes-side LO phonon bands are clearly seen in the PSHB spectra. The energy of the LO phonon was determined to be 17.4 meV by the PSHB method, which is lower than that in the bulk CuI crystals (18.7 meV) by 1.3 meV by 7% [11]. The LO phonon energy as a function of photon energy at the observed hole structure is shown in Fig. 5(c). We can estimate two anticrossing points where either $1p_e$-$1s_e$ energy spacing for electron quantum states or $1p_h$-$1s_h$ energy spacing for hole quantum states resonates with LO phonon energy on the model of strong confinement. Here we assume QDs are not perfectly spherical. Although we have not observed the exciton-phonon coupled states in the PSHB spectra, we could see small changes of the LO phonon energy at the expected anticrossing points.

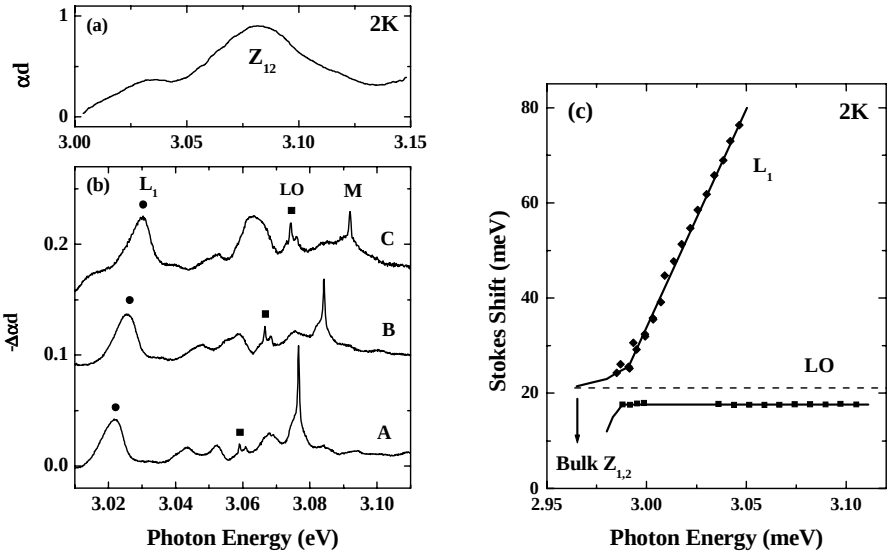

Figure 4. Absorption (a) and PSHB spectra (b) of CuBr QDs in NaBr crystals. The excitation energies for spectra A, B, and C are 3.0766, 3.0843, and 3.0916 eV, respectively. The excitation density is 100 nJ/cm^2 and exposure time is 3 minutes. (c). Stokes shifts of the satellite holes L_1 and LO as a function of observed photon energy of the respective hole structures. The dashed line shows the LO phonon energy in the bulk CuBr crystals. The solid lines show a guide for eyes.

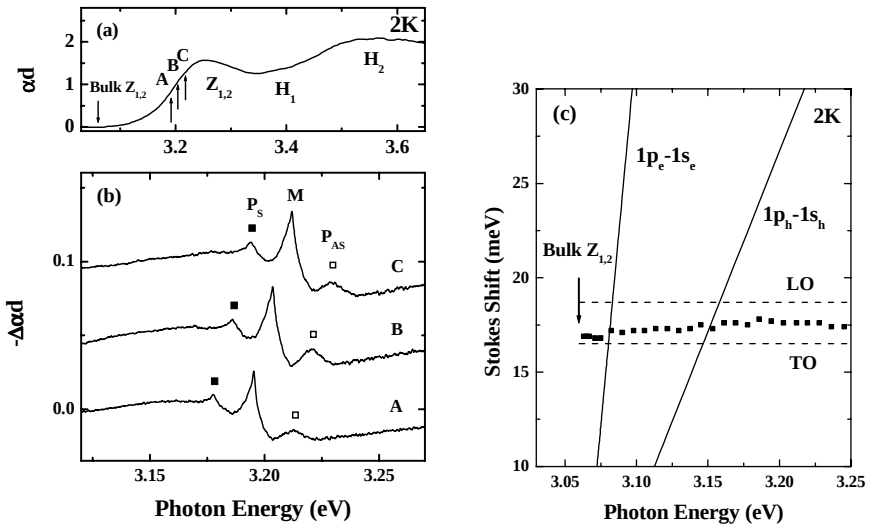

Figure 5. Absorption (a) and PSHB spectra (b) of CuI QDs in glass with an average radius of 2.8 nm. The excitation energies for spectra A, B, and C are 3.1954, 3.2036, and 3.2119eV, respectively. The excitation density is 100 nJ/cm^2 and exposure time is 5 minutes. (c) Stokes shift of LO phonon sideband and $1p_e$-$1s_e$ and $1p_h$-$1s_h$ energy spacings as a function of photon energy at the observed hole structure. The dashed lines show the LO and TO phonon energies in the bulk CuI crystal studied by Raman scattering.

Table 1. The energy softening and material parameters

	ε_0	ε_∞	κ	Ω (meV)$_{Raman}$	Ω^* (meV)$_{HB}$	- $\delta\Omega$(meV)
bulk CuCl	7.9	3.61	6.65	25.6		
CuCl QDs in glass				26.2	23.5	2.1
CuCl QDs in NaCl					23.1	2.5
bulk CuBr	7.9	4.06	8.36	21.1		
CuBr QDs in glass				20.3	18.6	2.5
CuBr QDs in NaBr					17.6	3.5
bulk CuI	6.5	4.58	15.5	18.7		
CuI QDs in glass					17.4	1.3

4.4. LO phonon softening in quantum dots

The above experimental results show that the energies of the LO phonons in CuBr QDs in glass and NaBr crystals as well as CuI QDs in glass were found to be 2.5 (12%), 3.5 (17%), and 1.3 meV (7%) lower than those in the bulk crystals. The reduction factors of the phonon energies agree with that (8%) observed in CuCl QDs in an order of magnitude. In our previous publication on the PSHB spectroscopy of CdTe QDs in glass [17], we note a small LO phonon softening by 8%, although the LO phonon structure is broader than the softening. The experimental data obtained in this work and our previous works are summarized in Table 1, together with their material parameters. Because the phonon softening factor $\delta\Omega/\Omega$ is inversely proportional to κ, those for CuCl QDs, CuBr QDs and CuI QDs are expected to be proportional to 1 : 0.75 : 0.43, but more stronger factor

depending on confinement type gives larger phonon softening factor to CuBr QDs and CuI QDs. The softening of the LO phonon energies are explained in terms of LO phonon renormalization by Fröhlich coupling with the exciton, electron or hole in the QDs and quantitative study of them should be investigated theoretically.

5. Conclusions

We have studied the excited state-LO phonons of CuBr QDs in glass and in NaBr crystals as well as CuI QDs in glass. The softening of the LO phonons was observed in CuBr and CuI QDs and was explained in terms of the phonon renormalization by Fröhlich coupling. These systematic observations of LO phonon softening together with our previous observation in CuCl QDs indicate the universality of LO phonon softening in small-sized QDs. The softening ranges from 7% to 17%. The phenomenon gives us a characteristic of QDs of their molecular nature. The phonon-exciton coupled states were clearly observed in CuBr QDs embedded in glass when the LO phonon energy is close to the energy difference between the ground and first excited state.

References

[1] Nakajima S, Toyozawa Y, and Abe R 1980 The Physics of Elementary Excitations (Springer, Berlin)
[2] Zimin L, Nair S V, and Masumoto Y 1998 Phys. Rev. Lett. 80 3105-3108
[3] Baranov A V, Yamauchi S, and Masumoto Y 2000 J. Lumin. 87-89 500-502
[4] Zhao J, Nair S V, and Masumoto Y 2001 Phys. Rev. B 63 033307-1-4
[5] Ohmura H, and Nakamura A 1999 Phys. Rev. B 59 12216-12219
[6] Fedorov A V, Baranov A V, Itoh A, and Masumoto Y 2001 Semicond. 35 1390-1397
[7] Nair S V and Masumoto Y 1999 Jpn. J. Appl. Phys. 38 581-584
[8] Nair S V, Zimin L, and Masumoto Y 1998 Proc. 24th Int. Conf. Physics of Semiconductors (Jerusalem), VII-B-63, pdf no.463
[9] Masumoto Y, Kawazoe T, and Yamamoto T 1995 Phys. Rev. B 52 4688-4691
[10] For the review of persistent spectral hole burning of quantum dots, see: Masumoto Y 1996 J. Lumin. 70 386-399, and Masumoto Y 2002 in Semiconductor Quantum Dots – Physics, Spectroscopy and Applications, ed. by Masumoto Y, and Takagahara T (Berlin: Springer) Chap. 5
[11] Physics of II-VI and I-VII Compounds, Semimagnetic Semiconductors, edited by O. Madelung, M. Schulz and H. Weiss, Landolt-Börnstein, New Series, Group III, Vol. 17, Pt. b (Springer, Berlin, 1982)
[12] Fedorov A V, Baranov A V, and Inoue K 1997 Phys. Rev. B 56 7491-7502
[13] Inoue K, Yamanaka A, Toba K, Baranov A V, Onushchenko A A, and Fedorov A V 1996 Phys. Rev. B 54 R8321-R8324
[14] Inoue K, Yamanaka A, Tanaka N, Baranov A V, and Fedorov A V 1998 J. Korean Phys. Soc. 32 S569-S571
[15] Baranov A V 2002 in Semiconductor Quantum Dots – Physics, Spectroscopy and Applications, ed. by Masumoto Y, and Takagahara T (Berlin: Springer) Chap. 7
[16] Masumoto Y, Kawabata K, and Kawazoe T 1995 Phys. Rev. B 52 7834-7837
[17] Masumoto Y and Sonobe K 1997 Phys. Rev. B 56 9734-9737